

# Optical Absorption Spectra of (Mg, Fe)SiO<sub>3</sub> Silicate Perovskites

Guoyin Shen<sup>1</sup>, Yingwei Fei<sup>2</sup>, Ulf Hålenius<sup>3</sup>, and Yanbin Wang<sup>4</sup>

<sup>1</sup> Theoretical Geochemistry Program, Inst. of Earth Sciences, Uppsala University, Norbyvägen 18B, 7526 3 Uppsala, Sweden

<sup>2</sup> Center for High Pressure Research, Geophysical Lab., Carnegie Inst. of Washington, 5251 Broad Branch Road, 20015, Washington DC, USA

<sup>3</sup> Dept. of Mineralogy, Swedish Museum of Natural History, Box 50007, 10405 Stockholm, Sweden

<sup>4</sup> Center for High Pressure Research, Department of Earth and Space Sciences, State University of New York at Stony Brook, 11794 New York, USA

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**Abstract.** Electronic absorption spectra have been measured at room temperature and pressure for polycrystalline samples of (Mg, Fe)SiO<sub>3</sub> silicate perovskites synthesized by multi-anvil device. One strong near-infrared band at about 7000 cm<sup>-1</sup> and several weak bands in the visible region were found. The near-infrared band at 7000 cm<sup>-1</sup> is assigned to a spin-allowed transition of Fe<sup>2+</sup> at the 8–12 coordinated site in perovskite. However, definite assignments of the weak bands in the visible region are difficult because of their low intensities and the scattering effect at the grain boundaries. Crystal field calculations for Fe<sup>2+</sup> at different sites in perovskite have been carried out based on the crystal structure data. The results agree with the assignment of Fe<sup>2+</sup> to the 8–12 coordinated site in perovskite. Crystal field stabilization energy of Fe<sup>2+</sup> with coordination number of 8 in perovskite is 3332 cm<sup>-1</sup> which is small compared to the octahedral site of magnesiowüstite (4320 cm<sup>-1</sup>), another important lower-mantle mineral.

## Introduction

Silicate perovskite is generally believed to be the most abundant mineral in the Earth's lower mantle, which accounts for more than half of the total volume of the Earth. Among the constituent cations, iron is the dominant transition metal and plays an important role in physical processes, such as electrical and thermal conduction. Therefore, the crystal chemistry of iron in perovskite is important for understanding properties of the Earth's mantle.

Single-crystal X-ray diffraction studies of MgSiO<sub>3</sub> with orthorhombic perovskite structure have shown that the octahedral site is filled with Si and SiO<sub>6</sub>-polyhedron is close to an ideal octahedron, while Mg occupies the 12-coordinated site and the position of Mg atom deviates from the center of the MgO<sub>12</sub> polyhedron resulting in that the Mg–O distances and O–Mg–O angles range widely from 2.01 to 3.12 Å and from 50.0 to 70.9°, respec-

tively (e.g., Horiuchi et al. 1987; Ross and Hazen 1990). The point symmetry of Mg-site is C<sub>s</sub>. The effective coordination number of Mg in MgSiO<sub>3</sub> perovskite varies from 8 to 12 with the degrees of distortion at different conditions.

With iron-containing samples, many observations concern the nature of iron in the structure. Using extended X-ray absorption fine structure (EXAFS) spectroscopy, Jackson et al. (1987) examined (Mg, Fe)SiO<sub>3</sub> perovskite synthesized at 50 GPa and 2000 K by laser-heated diamond anvil cell and concluded that some Fe substitutes for Si in the octahedral site and, by inference, some of the Si is present in the 8–12 coordinated site. The Mössbauer data of Jeanloz et al. (1991) also imply that Fe occupies the octahedral site. However, using (Mg, Fe)SiO<sub>3</sub> perovskite synthesized by multi-anvil device, Parise et al. (1990) pointed out that Fe is in a more distorted site in the perovskite than in enstatite based on the structural refinement and the measurement of X-ray absorption near the Fe K-edge, and concluded that Fe substitutes for Mg in the 8–12 coordinated site. The single-crystal structure refinement by Kudoh et al. (1990) indicates that Fe substitutes for Mg rather than Si. Mössbauer data (McCammon et al. 1992) show, at 298 K, a dominant absorption doublet which was assigned to Fe<sup>2+</sup> in the 8–12 coordinated site. The Mössbauer data of Fei et al. (1993) also indicate the occupancy of Fe in the distorted 8–12 coordinated site.

Optical absorption spectroscopy is sensitive to the local environment of a transition metal ion and is a suitable method to study the nature of Fe in the silicate perovskite. Furthermore, the optical spectra provide information on the crystal-field stabilization energy (CFSE) which has a strong effect on the partitioning of Fe<sup>2+</sup> between the perovskite and its coexisting phases, such as magnesiowüstite, in the Earth's lower mantle (Yagi et al. 1978; Burns 1985, 1993). Heinz and Jeanloz (1987) measured the absorption coefficient between 23800 cm<sup>-1</sup> and 11000 cm<sup>-1</sup> for the (Mg<sub>0.90</sub>Fe<sub>0.10</sub>)SiO<sub>3</sub> perovskite synthesized by laser-heated diamond anvil cell. Their purpose of the measurement was to check

the absorption of the sample to the YAG laser light (10640 Å); and no band was resolved in their measurement. Burns (1993) has predicted approximate locations of absorption bands in silicate perovskites for  $\text{Fe}^{2+}$  at the 8–12 coordinated site. There is, so far, no experimental optical absorption bands reported for  $(\text{Mg}, \text{Fe})\text{SiO}_3$  silicate perovskite. In this paper, we report the first optical absorption data of  $(\text{Mg}, \text{Fe})\text{SiO}_3$  silicate perovskites synthesized by multi-anvil device.

## Experimental Procedure

Two polycrystalline  $(\text{Mg}, \text{Fe})\text{SiO}_3$  silicate perovskite samples with  $\text{Fe}/(\text{Fe} + \text{Mg})$  ratios of 0.05 and 0.10 were synthesized at 26 GPa and at 1873 K in the multi-anvil apparatus at Stony Brook, New York. The starting material were  $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{SiO}_3$  and  $(\text{Mg}_{0.90}\text{Fe}_{0.10})\text{SiO}_3$  enstatites which were synthesized in piston-cylinder apparatus at 2 GPa and 1273 K. The final products were examined by powder X-ray diffraction, showing that both samples were in a single phase of orthorhombic perovskites with the unit cell volumes for the  $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{SiO}_3$  and  $(\text{Mg}_{0.90}\text{Fe}_{0.10})\text{SiO}_3$  perovskites are 162.80(1) and 163.0(1) Å<sup>3</sup>, respectively. Their bulk compositions determined with the electron microprobe are  $\text{Mg}_{0.951(7)}\text{Fe}_{0.050(5)}\text{Si}_{0.999(4)}\text{O}_3$  and  $\text{Mg}_{0.906(1)}\text{Fe}_{0.100(6)}\text{Si}_{0.997(5)}\text{O}_3$ . Mössbauer absorption bands (Fei et al. 1993) revealed the presence of 12%  $\text{Fe}^{3+}$  of total iron in the samples, and no bands were attributed to the other iron-bearing phases. The grain size of the polycrystalline samples ranges from 0.5 to 2 µm in diameter. The colour of the samples are mainly dominated by scattering at the grain boundaries. The samples are approximately 150 µm in linear dimensions and were polished to about 30–50 µm thickness. In the polishing process, the samples were slowly polished by hand on diamond powder to avoid the possible amorphization, since the  $(\text{Mg}, \text{Fe})\text{SiO}_3$  perovskite is a metastable phase at ambient pressure. Samples were mounted in glycerine on a glass slide for optical spectral measurements.

Unpolarized optical absorption spectra were measured by means of an automated Zeiss MPM800 microscope-spectropho-

tometer at the Swedish Museum of Natural History, using Zeiss ultrafluar 20× as objective and 10× as condenser. Measuring spots were 20 µm in diameter with air as reference. Light sources were a 75 W Xenon lamp in the uv-vis region and a halogen 100 W lamp in the near-infrared. In the range 12 500–30 000 cm<sup>-1</sup> a photomultiplier served as detector and below 12 500 cm<sup>-1</sup> a PbS-cell was used. The spectral bandwidths as well as step widths were 1 nm and 5 nm in the visible and near-infrared ranges respectively.

## Experimental Results

Optical absorption spectra in the range of 27 000–5000 cm<sup>-1</sup> for  $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{SiO}_3$  (spectrum **a**) and  $(\text{Mg}_{0.90}\text{Fe}_{0.10})\text{SiO}_3$  (spectrum **b**) perovskites are shown in Figure 1. A near-infrared band is clearly resolved at about 7000 cm<sup>-1</sup> in spectrum **a**, while a shoulder at the same region is seen in spectrum **b**. No further band was found when we measured down to 4600 cm<sup>-1</sup>. In the visible region, there are several bands superposed on the background absorption which displays an anomalous distribution. It indicates possible scattering effects due to the grain boundaries presence in the measured sample area. The bands in the visible region are, thus, not well resolved.

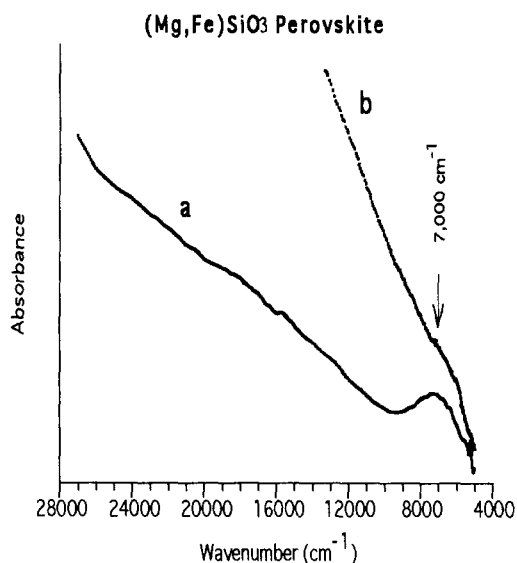
The increase of absorbance towards the visible region in spectrum **b** is more than that in spectrum **a**. However, this is not always the case for the two samples. The absorbance from different area of one sample was found to have different intensities because of the different grain distributions of the measured sample area. When the background absorbance in the visible is relatively weak, it is possible to get a well resolved band at near-infrared region (spectrum **a**); otherwise the near-infrared band is superposed on the background, showing a shoulder (spectrum **b**). Thinning the sample further down (about 20 µm thickness) could not improve the quality of the spectra; and, in some cases, the near-infrared band at 7000 cm<sup>-1</sup> turned to be very weak or even disappear after thinning due to the possible amorphization during polishing.

## Discussions

### Crystal Field Calculation

Since the spectra show near-infrared bands which could be due to the spin-allowed transitions of  $\text{Fe}^{2+}$  in the crystal. Crystal field theory has been used to calculate the energy levels of  $\text{Fe}^{2+}$  in the perovskite based on its crystal structure. Silicate perovskite,  $(\text{Mg}, \text{Fe})\text{SiO}_3$ , has an orthorhombic perovskite-type crystal structure *Pbnm* with 4 formula units per cell (e.g., Horiuchi et al. 1987; Ross and Hazen 1990). In the structure,  $\text{SiO}_6$  is close to an ideal octahedron in which the Si–O distances and O–Si–O angles are nearly equal; their values range from 1.779 to 1.801 Å and from 88.2 to 91.0°, respectively. However, the  $\text{MgO}_6$  polyhedron has a large distortion with the Mg–O distances and O–Mg–O angles ranging widely from 2.009 to 3.111 Å and from 50.0 to 70.9°, respectively (Ross and Hazen 1990).

$\text{Fe}^{2+}$ –O bonding in silicates is usually rather ionic compared with iron-sulfur bonding. The predominant contributions to the crystal field in silicates appear to arise from the ions in the first coordination sphere (e.g., Huggins 1975). Therefore the nearest point-charge model has been adopted for calculating the spin-allowed energy levels of  $\text{Fe}^{2+}$  in silicate perovskites (Griffith 1961). The Hamiltonian matrix elements can be obtained as long



**Fig. 1a, b.** The optical absorption spectra for  $(\text{Mg}, \text{Fe})\text{SiO}_3$  perovskite samples synthesized by multi-anvil device: **a**  $(\text{Mg}_{0.95}\text{Fe}_{0.05})\text{SiO}_3$ , **b**  $(\text{Mg}_{0.90}\text{Fe}_{0.10})\text{SiO}_3$ . The absorbance is not normalized for both spectra because of the different thickness and polycrystalline nature of samples. The absorbance from different area of one sample was found to have different intensities

**Table 1.** Calculated spin-allowed transitions for  $\text{Fe}^{2+}$  at different sites in perovskites

Site	8–12 coordinated site			Octahedral site
	8	10	12	6
C.N. <sup>a</sup>	8	10	12	6
effective charge <sup>b</sup>	−1.53	−1.25	−1.25	−0.63
transition <sup>c</sup>	7023	7034	7050	7050
	4432	4783	4951	6761
	4198	3026	3504	100
	404	735	595	57

<sup>a</sup> C.N. denotes coordination number. Coordinates were chosen according to the bond lengths

<sup>b</sup> Effective charge of oxygen ion. Pure ionic state means effective charge of −2.0

<sup>c</sup> Energy is in wavenumber ( $\text{cm}^{-1}$ ). The transition order was arranged according to the energy values

**Table 2.** Observed near-infrared bands for  $\text{Fe}^{2+}$  in silicate perovskite, periclase, and garnet structures

Mineral	Site	Coordination number	Bondlength (Å)	Band ( $\text{cm}^{-1}$ )
silicate	A	6	1.78–1.80 <sup>a</sup>	
perovskite	B	8–12	2.01–3.11 <sup>a</sup>	7000 <sup>c</sup>
periclase	6	6	2.11 <sup>b</sup>	11600 <sup>d</sup> 10000 <sup>d</sup>
garnet	D <sub>2</sub>	8	2.20–2.34 <sup>b</sup>	7800 <sup>e</sup> 6100 <sup>e</sup> 4500 <sup>e</sup>

<sup>a</sup> Ross and Hazen (1990)

<sup>b</sup> Smyth and Bish (1988)

<sup>c</sup> This study

<sup>d</sup> Goto et al. (1980)

<sup>e</sup> White and Moore (1972)

as we know the geometric parameters  $\gamma_{ka}^{(b)}$  (see Appendix) that are determined by crystallographic data (Ross and Hazen 1990). Then we can get the spin-allowed transitions of  $\text{Fe}^{2+}$  at different sites in perovskites. The results are given in Table 1.

### Iron in Perovskite

The near-infrared bands for the perovskite samples are compared in Table 2 with the corresponding spin-allowed bands of  $\text{Fe}^{2+}$  for periclase, and garnet structures. In the  $\text{MgSiO}_3$  perovskite structure, the octahedral site is rather symmetric and the mean bond distance is significantly smaller in perovskite than in the other ferromagnesian silicates and oxides. The energy splitting of the  $^5E_g$  state of  $\text{Fe}^{2+}$  in symmetric octahedral site should be small; and the shorter bond distance generally result in that the  $^5E_g$  states of  $\text{Fe}^{2+}$  would be of higher energy values, possibly more than  $12000 \text{ cm}^{-1}$ . Furthermore, according to our crystal field calculation, the effective charge, the only adjustable parameter which reflects the extent of ionicity of the bonding, of −0.63 was required

for octahedral site to fit the data. This value is unusually small. The effective charge values of oxygen range approximately from −1.2 to −1.9 for many silicates (Sasaki et al. 1982). For  $\text{Fe}^{2+}$  containing silicate garnets, the effective charge of −1.88 was given to have a satisfactory agreement with experimental data (Shen and Zhao 1984). We, therefore, conclude that the near-infrared band at  $7000 \text{ cm}^{-1}$  is not due to the spin-allowed transition of  $\text{Fe}^{2+}$  at octahedral site in the  $(\text{Mg, Fe})\text{SiO}_3$  perovskite.

Instead, the location of the near-infrared band at  $7000 \text{ cm}^{-1}$  of  $(\text{Mg, Fe})\text{SiO}_3$  perovskite is consistent with the region of spin-allowed bands of  $\text{Fe}^{2+}$  in 8-coordinated sites in ferromagnesian silicates, such as garnets (see Table 2). By noting that the average metal-oxygen distances to the eight nearest-neighbour oxygens in 8–12 coordinated site are comparable to those in pyrope-almandine garnets, Burns (1993) predicted the approximate locations of absorption bands for  $(\text{Mg, Fe})\text{SiO}_3$  perovskite in the region  $4500\text{--}8000 \text{ cm}^{-1}$ . The present data support his prediction. It is also shown in our calculation that, for the 8–12 coordinated site, the effective charge values for different coordination number range from −1.25 to −1.53 which are not inconsistent with many other mantle silicate minerals. Therefore, we assign  $\text{Fe}^{2+}$  to 8–12 coordinated site in perovskite. The assignment is also consistent with the conclusions from X-ray absorption near-edge spectroscopy (Parise et al. 1990), single crystal X-ray refinement (Kudoh et al. 1990), and Mössbauer data (McCammon et al. 1992; Fei et al. 1993).

Note that in Table 1 the second transition values are  $4432$ ,  $4783$  and  $4951 \text{ cm}^{-1}$  with coordination number of 8, 10 and 12 respectively. Since no further band down to  $4600 \text{ cm}^{-1}$  was resolved in the experiment, and no transition is symmetry-forbidden for the point symmetry  $C_s$ , 8–12 coordinated site in perovskite at our experimental conditions (polycrystalline samples, unpolarized light source), we may consider the calculation result with coordination number 8 as a better fit to experimental data. However, it is difficult to conclude the exact coordination number of  $\text{Fe}^{2+}$  in perovskite from the present data. The effective coordination number in perovskite is related to the distortion of the structure (Marezio et al. 1970). Different conditions of temperature and pressure, and possibly of sample synthesis could affect the degrees of distortion of the structure (Wang et al. 1992).

Mössbauer data (Fei et al. 1993) revealed that the molar  $\text{Fe}^{3+}/\Sigma\text{Fe}$  is about  $0.12(\pm 0.02)$  and  $\text{Fe}^{3+}$  is ordered in a single octahedral site for both samples used for present study. Since the octahedra and 8–12 coordinated polyhedra share all of their edges with each other with the shortest M–M distance of only  $2.79 \text{ Å}$ , Burns (1993) predicted a broad  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  intervalence charge transfer band in the  $14000\text{--}16000 \text{ cm}^{-1}$  region. From the spectrum a of Fig. 1, superimposed on the background is a weak broad absorption envelope at the region  $15000\text{--}19000 \text{ cm}^{-1}$ . But, a definite assignment for the broad envelope could not be reached due to the anomalous distribution of the background. Using single crystals or large grain polycrystalline samples would sur-

ely improve the quality of the spectra. Therefore, more optical absorption spectroscopy measurements are needed to have well-resolved bands in the uv-vis region to study the crystal chemistry of  $\text{Fe}^{3+}$  in perovskite and the electron hopping between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , since some geophysically significant properties of lower mantle minerals probably result from defect  $\text{Fe}^{3+}$  (Sherman 1991; Fei et al. 1993).

### Crystal-Field Stabilization Energy

The importance of crystal field effects in the perovskite structure derives from the fact that the *CFSE* of  $\text{Fe}^{2+}$  at the 8–12 coordinated site is predicted to have the lower value compared to that at octahedral site (Burns 1993). Thus iron is less stable in the silicate perovskite and will tend to partition to mineral phases that have sites with higher *CFSE*, such as the octahedral site in magnesiowüstite. Based on the optical absorption data and the crystal field calculation result as shown in Table 1, the *CFSE* of  $\text{Fe}^{2+}$  in perovskite with coordination number of 8 was calculated as  $3332 \text{ cm}^{-1}$  which is really small compared to that of magnesiowüstite ( $4320 \text{ cm}^{-1}$ , Goto et al. 1980). In investigations of iron partitioning in the system  $\text{MgO}-\text{FeO}-\text{SiO}_2$  at high pressures and temperatures, compositions  $(\text{Mg}_{1-x}\text{Fe}_x)_2\text{SiO}_4$  yielded magnesiowüstite with higher Fe/Mg ratios than coexisting perovskites (e.g., Ito et al. 1984; Fei et al. 1991). Higher *CFSE* of  $\text{Fe}^{2+}$  in periclasite structure favours the concentration of iron in magnesiowüstite and depletion of iron in a coexisting perovskite phase. Evidently, the optical spectra of these two minerals at high pressures and temperatures would give the *CFSE* at those conditions which will provide informations on the trend of the iron partitioning between silicate perovskite and magnesiowüstite at different levels of the Earth's lower mantle. Moreover, at deep mantle conditions, there may be the high spin/low spin transition of  $\text{Fe}^{2+}$  and the structural phase transitions (Burns 1993). Such kinds of phase transitions would strongly affect the iron partition among lower mantle phases. Optical absorption spectroscopy on lower mantle minerals at very high pressures and temperatures could reflect the change of the local environment of iron and provide useful informations on the electronic properties of iron in crystals and the iron partitioning between lower mantle minerals.

### Conclusion

We conclude the following based on our optical absorption data and crystal field analysis for silicate perovskites:

1.  $\text{Fe}^{2+}$  occupies the 8–12 coordinated site in perovskite.
2. The *CFSE* of  $\text{Fe}^{2+}$  in perovskite with coordination number of 8 is calculated as  $3332 \text{ cm}^{-1}$ , which is small compared to that of magnesiowüstite ( $4320 \text{ cm}^{-1}$ ).

### Appendix

The one-electron crystal-field potential can be written as:

$$V_i = \sum_{k=2,4} \sum_{a,b} r^k \gamma_{ka}^{(b)} Z_{ka}^{(b)}(\theta_i, \phi_i) \\ = -(\gamma_{20} Z_{20} + \sqrt{3} \gamma_{22}^c Z_{22}^c + \sqrt{3} \gamma_{22}^s Z_{22}^s) \sqrt{\frac{\pi}{5}} e^2 r^2 \\ -(\gamma_{40} Z_{40} + 2\sqrt{5} \gamma_{42}^c Z_{42}^c + 2\sqrt{5} \gamma_{42}^s Z_{42}^s \\ + \sqrt{35} \gamma_{44}^c Z_{44}^c + \sqrt{35} \gamma_{44}^s Z_{44}^s) \frac{\sqrt{\pi}}{12} e^2 r^2,$$

where  $Z_{ka}^{(b)}(\theta_i, \phi_i)$  denotes real spherical harmonic functions;  $r_i, \theta_i, \phi_i$  are the coordinates of the  $d$  electrons in  $\text{Fe}^{2+}$ ;  $e$  denotes the electron charge; and  $\gamma_{ka}^{(b)}$  (Griffith 1961) are geometric parameters that can be determined by crystal structure data.

$\text{Fe}^{2+}$ , with  $3d^6$  configuration, is thus subject to the crystal-field potential:

$$V = \sum_{i=1}^6 V_i.$$

Since only spin-allowed transitions are considered, the system can be treated as one electron system. We obtain the Hamiltonian matrix elements of the quintet state ( $5 \times 5$  matrix) as follows:

$$\begin{aligned} H_{xy,xy} &= 24 \left[ \left( 5\gamma_{44}^c - \frac{\gamma_{40}}{7} \right) \langle r^4 \rangle + \frac{24}{7} \gamma_{20} \langle r^2 \rangle \right] e^2; \\ H_{xy,xz} &= 0; \quad H_{xy,yz} = 0; \\ H_{xy,x^2-y^2} &= -\frac{5}{24} \gamma_{44}^s \langle r^4 \rangle e^2; \\ H_{xy,z^2} &= \left( -\frac{5\sqrt{3}}{84} \gamma_{42}^s \langle r^4 \rangle + \frac{\sqrt{3}}{7} \gamma_{22}^s \langle r^2 \rangle \right) e^2; \\ H_{xz,xz} &= 42 [(-5\gamma_{42}^c + \gamma_{40}) \langle r^4 \rangle \\ &\quad - (9\gamma_{22}^c + 3\gamma_{20}) \langle r^2 \rangle] e^2; \\ H_{xz,yz} &= 42 (-5\gamma_{42}^s \langle r^4 \rangle - 9\gamma_{22}^s \langle r^2 \rangle) e^2; \\ H_{xz,x^2-y^2} &= 0; \quad H_{xz,z^2} = 0; \\ H_{yz,yz} &= 42 [(5\gamma_{42}^c + \gamma_{40}) \langle r^4 \rangle + (9\gamma_{22}^c - 3\gamma_{20}) \langle r^2 \rangle] e^2; \\ H_{yz,x^2-y^2} &= 0; \quad H_{yz,z^2} = 0; \\ H_{x^2-y^2,x^2-y^2} &= 24 \left[ \left( -5\gamma_{44}^c - \frac{\gamma_{40}}{7} \right) \langle r^4 \rangle + \frac{24}{7} \gamma_{20} \langle r^2 \rangle \right] e^2; \\ H_{x^2-y^2,z^2} &= \left( -\frac{5\sqrt{3}}{84} \gamma_{42}^c \langle r^4 \rangle + \frac{\sqrt{3}}{7} \gamma_{22}^c \langle r^2 \rangle \right) e^2; \\ H_{z^2,z^2} &= -28 (\gamma_{40} \langle r^4 \rangle + 4\gamma_{20} \langle r^2 \rangle) e^2; \end{aligned}$$

where  $xy, xz, yz, x^2-y^2$  and  $z^2$  denote five  $d$ -orbitals;  $\langle r^2 \rangle$  and  $\langle r^4 \rangle$  are the expectation values with  $\langle r^2 \rangle = 2.2949 \text{ a.u.}$  and  $\langle r^4 \rangle = 14.0 \text{ a.u.}$ , calculated from the  $d$ -orbital for  $\text{Fe}^{2+}$  (Zhao and Du 1983);  $\gamma_{ka}^{(b)}$  are deter-

mined by crystallographic data (Ross and Hazen 1990);  $e$  denotes the effective charge of the oxygen. Therefore, the energy values of the spin-allowed transitions for  $\text{Fe}^{2+}$  can be obtained with only one adjustable parameter, the effective charge.

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